

An Improved System for the Palladium-Catalyzed Borylation of Aryl Halides with Pinacol Borane

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Experimental Section

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General Considerations. All reactions were stirred with the aid of a magnetic stirrer and carried out under an argon atmosphere. 1,4-Dioxane (anhydrous), triethylamine ($\geq 99.5\%$) and pinacol borane (97%) were purchased from Aldrich Chemical Co. in SureSeal® bottles. Commercially available materials were used without further purification unless otherwise noted. SPhos (**1**) and aryl halides were purchased from Aldrich Chemical Co. Liquid aryl halides were purified by passage through a pad of basic alumina prior to use. $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ was purchased from Strem Chemicals, Inc. and stored in a benchtop desiccator.

All new compounds were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy, melting points (for solids) and, in some cases, elemental analysis. Known compounds were characterized by ^1H NMR, ^{13}C NMR and melting points (for solids) and compared to their literature values. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300. Infrared spectra were recorded on an ASI Applied Systems ReactIR 1000 (neat samples were placed directly on the DiComp probe). Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. All ^1H NMR experiments are reported in δ units, parts per million (ppm) downfield of TMS and were measured relative to the signals for the residual benzene (7.16 ppm), chloroform (7.26 ppm), dimethylsulfoxide

(2.50 ppm) or methanol (3.31 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual chloroform (77 ppm), dimethylsulfoxide (39.5 ppm) or methanol (49 ppm) and were obtained with ^1H decoupling. Melting points were obtained on a Mel-Temp capillary melting point apparatus and are uncorrected. Gas chromatographic analyses were performed on Hewlett-Packard 6890 gas chromatography instrument with a FID detector using 25 m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase.

The yields in table 2 refer to isolated yields (average of two runs) of compounds estimated to be $\geq 95\%$ pure as determined by ^1H NMR and GC analysis and/or combustion analysis.

I. Experimental for the Borylation of Aryl Halides.

General Procedure A: Pd-Catalyzed Borylation of Aryl Iodides and Bromides.

An oven-dried resealable Schlenk tube possessing a Teflon screw valve was charged with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (0.25%-2.0%) and SPhos (1.0-8.0%). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was carried out a total of two times). 1,4-Dioxane (0.30 mL) was added via syringe, through the septum, followed by the addition of the aryl halide (0.50 mmol), NEt_3 (0.209 mL, 152 mg, 1.50 mmol) and pinacol borane (0.109 mL, 96.1 mg, 0.75 mmol) in a like manner (aryl halides that were solids were added with the other solid reagents). The septum was then replaced with a Teflon screw valve and the Schlenk tube was sealed. The reaction mixture was heated to 110 °C (*These reactions are conducted in a sealed tube at a temperature higher than the boiling point of 1,4-dioxane and NEt_3 . For larger scale reactions, the appropriate safety precautions should be undertaken including the use of a blast shield*) until the aryl halide had been completely consumed as determined by gas chromatography and the reaction mixture was then allowed to cool to room temperature. The reaction solution was filtered through a thin pad of celite (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via flash chromatography on silica gel.

General Procedure B: Pd-Catalyzed Borylation of Aryl Chlorides.

An oven-dried resealable Schlenk tube possessing a Teflon screw valve was charged with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (3.0-4.0%) and SPhos (12.0-16.0%). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was carried out a total of two times). NEt_3 (0.500 mL) was added via syringe, through the septum, followed by the addition of the aryl chloride (0.50 mmol) and pinacol borane (0.109 mL, 96.1 mg, 0.75 mmol) in a like manner (aryl halides that were solids were added with the other solid reagents). The septum was then replaced with a Teflon screw valve and the Schlenk tube was sealed. The reaction mixture was heated to 110 °C (*These reactions are conducted in a sealed tube at a temperature higher than the boiling point of 1,4-dioxane and NEt_3 . For larger scale reactions, the appropriate safety precautions should be undertaken (i.e. the use of a blast shield)*) until the aryl halide had been completely consumed as determined by gas chromatography and was then allowed to cool to room temperature. The reaction solution was filtered through a thin pad of celite (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via flash chromatography on silica gel.

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 1).¹

Following general procedure A, a mixture of 4-iodoanisole (127 mg, 0.50 mmol), pinacol borane, NEt_3 , $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (1.3 mg, 0.0050 mmol) and SPhos (8.2 mg, 0.020 mmol) was heated in 1,4-dioxane for 30 min. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 110 mg (94% yield) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ : 7.75 (d, J = 9 Hz, 2H), 6.90 (d, J = 9 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ : 162.1, 136.4, 113.2, 102.7, 83.4, 55.0, 24.8. ^1H NMR spectrum included.

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 2).¹

Following general procedure A on a larger scale, a mixture of 4-iodoanisole (234 mg, 1.00 mmol), pinacol borane (0.218 mL, 192 mg, 1.50 mmol), NEt_3 (0.418 mL, 354 mg, 3.00 mmol), $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (0.26 mg, 0.0010 mmol) and SPhos (1.6 mg, 0.0040 mmol) was heated in 1,4-dioxane for 30 min. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 212 mg (91 % yield) as a colorless oil.

¹ Zhu, W.; Ma, D. *Org. Lett.* **2006**, 8, 261.

¹H NMR (300 MHz, CDCl₃) δ: 7.75 (d, J = 9 Hz, 2H), 6.90 (d, J = 9 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 162.1, 136.4, 113.2, 102.7, 83.4, 55.0, 24.8. ¹H NMR spectrum included.

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 3).¹

Following general procedure A, a mixture of 4-bromoanisole (62.5 μL, 93.5 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (1.3 mg, 0.0050 mmol) and SPhos (8.2 mg, 0.020 mmol) was heated in 1,4-dioxane for 1 h. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 113 mg (97% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.75 (d, J = 9 Hz, 2H), 6.90 (d, J = 9 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 162.1, 136.4, 113.2, 102.7, 83.4, 55.0, 24.8. ¹H NMR spectrum included.

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 4).¹

Following general procedure B, a mixture of 4-chloroanisole (61.2 μL, 71.3 mg, 0.50 mmol), pinacol borane, NEt₃ (0.500 mL), PdCl₂(CH₃CN)₂ (3.9 mg, 0.015 mmol) and SPhos (24.6 mg, 0.060 mmol) was heated for 24 h. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 112 mg (96% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.75 (d, J = 9 Hz, 2H), 6.90 (d, J = 9 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 162.1, 136.4, 113.2, 102.7, 83.4, 55.0, 24.8. ¹H NMR spectrum included.

***N,N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, Entry 5).²**

Following general procedure A, a mixture of 4-bromo-*N,N*-dimethylaniline (100.0 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (1.3 mg, 0.0050 mmol) and SPhos (8.2 mg, 0.020 mmol) was heated in 1,4-dioxane for 3 h. Recrystallization (Hexanes) yielded the title compound in 105 mg (85% yield) as a white solid, mp 116-117 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.71 (d, J = 8 Hz, 2H), 6.70 (d, J = 8 Hz, 2H), 3.00 (s, 6H), 1.34 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 152.5, 136.1, 111.2, 83.1, 40.1, 24.8 (No C-B Signal). ¹H NMR spectrum included.

² Broutin, P.-E.; Cerna, I.; Campaniello, M.; Leroux, F.; Colobert, F. *Org. Lett.* **2004**, *6*, 4419.

2-(4-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 6).³

Following general procedure A, a mixture of 4-bromo-*n*-butylbenzene (106.5 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (1.3 mg, 0.0050 mmol) and SPhos (8.2 mg, 0.020 mmol) was heated in 1,4-dioxane for 4 h. Flash column chromatography (2.5% EtOAc/Hexanes) yielded the title compound in 109 mg (84% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.75 (d, J = 8 Hz, 2H), 7.22 (d, J = 8 Hz, 2H), 2.64 (t, J = 8 Hz, 2H), 1.62 (p, J = 8 Hz, 2H), 1.37 (sex, J = 8 Hz, 2H), 1.36 (s, 12H), 0.94 (t, J = 8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 146.3, 134.8, 127.9, 83.5, 35.8, 33.5, 24.8, 22.3, 13.9 (No C-B Signal). ¹H NMR spectrum included.

2-(4-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 7).³

Following general procedure B, a mixture of 4-*n*-butylchlorobenzene (82.0 μL, 84.4 mg, 0.50 mmol), pinacol borane, NEt₃ (0.50 mL), PdCl₂(CH₃CN)₂ (3.9 mg, 0.015 mmol) and SPhos (24.6 mg, 0.060 mmol) was heated in 1,4-dioxane for 24 h. Flash column chromatography (2.5% EtOAc/Hexanes) yielded the title compound in 81 mg (62% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.75 (d, J = 8 Hz, 2H), 7.22 (d, J = 8 Hz, 2H), 2.64 (t, J = 8 Hz, 2H), 1.62 (p, J = 8 Hz, 2H), 1.37 (sex, J = 8 Hz, 2H), 1.36 (s, 12H), 0.94 (t, J = 8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 146.3, 134.8, 127.9, 83.5, 35.8, 33.5, 24.8, 22.3, 13.9 (No C-B Signal). ¹H NMR spectrum included.

phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (Table 1, Entry 8).⁴

Following general procedure A, a mixture of 4-bromobenzophenone (130 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (1.3 mg, 0.0050 mmol) and SPhos (8.2 mg, 0.020 mmol) was heated in 1,4-dioxane for 5 h. Flash column chromatography (10% EtOAc/Hexanes) yielded the title compound in 108 mg (70% yield) as a yellow solid, mp 96-97 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.91 (d, J = 8 Hz, 2H), 7.79 (dd, J = 1,8 Hz, 2H), 7.76 (d, J = 8 Hz, 2H), 7.59 (dt, J = 1,8 Hz, 1H), 7.48 (t, J = 8 Hz, 2H), 1.37 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 196.9, 139.7, 137.4, 134.5, 132.5, 130.1, 129.0, 128.3, 84.2, 24.9 (No C-B Signal). ¹H NMR spectrum included.

³ Laza, C.; Duñach, E. *Adv. Synth. Catal.* **2003**, 345, 580.

⁴ Fürstner, A.; Seidel, G. *Org. Lett.* **2002**, 4, 541.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (Table 1, Entry 9).⁵

Following general procedure A, a mixture of 3-bromobenzonitrile (91 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (1.3 mg, 0.0050 mmol) and SPhos (8.2 mg, 0.020 mmol) was heated in 1,4-dioxane for 3 h. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 65 mg (57% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 8.08 (s, 1H), 7.99 (d, J = 7 Hz, 1H), 7.71 (d, J = 7 Hz, 1H), 7.46 (t, J = 7 Hz, 1H), 1.34 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 138.7, 138.4, 134.4, 128.4, 118.8, 112.0, 84.4, 24.8 (No C-B Signal). ¹H NMR spectrum included.

2-(2-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 10).²

Following general procedure A, a mixture of 2-bromoanisole (62.3 μL, 93.5 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (2.6 mg, 0.010 mmol) and SPhos (16.4 mg, 0.040 mmol) was heated in 1,4-dioxane for 4 h. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 104 mg (89% yield) as a white solid, mp 77-78 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.67 (dd, J = 7,2 Hz, 1H), 7.39 (dt, J = 8,2 Hz, 1H), 6.94 (dt, J = 7,2 Hz, 1H), 6.85 (d, J = 8 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 164.8, 137.4, 133.2, 120.9, 111.1, 84.1, 56.5, 25.5 (No C-B Signal). ¹H NMR spectrum included.

2-(2-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 11).²

Following general procedure B, a mixture of 2-chloroanisole (62.3 μL, 93.5 mg, 0.50 mmol), pinacol borane, NEt₃ (0.50 mL), PdCl₂(CH₃CN)₂ (5.2 mg, 0.020 mmol) and SPhos (32.8 mg, 0.080 mmol) was heated for 24 h. Flash column chromatography (5.0% EtOAc/Hexanes) yielded the title compound in 60 mg (51% yield) as a white solid, mp 76-77 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.67 (dd, J = 7,2 Hz, 1H), 7.39 (dt, J = 8,2 Hz, 1H), 6.94 (dt, J = 7,2 Hz, 1H), 6.85 (d, J = 8 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 164.8, 137.4, 133.2, 120.9, 111.1, 84.1, 56.5, 25.5 (No C-B Signal). ¹H NMR spectrum included.

2-mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 12).⁶

Following general procedure A, a mixture of 2-bromomesitylene (76.5 μL, 99.5 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (2.6 mg, 0.010 mmol) and SPhos (16.4 mg, 0.040

⁵ Zhu, L.; Duquette, J.; Zhang, M. *J. Org. Chem.* **2003**, *68*, 3729.

⁶ Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508.

mmol) was heated in 1,4-dioxane for 4 h. Flash column chromatography (2.5% EtOAc/Hexanes) yielded the title compound in 111 mg (90% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 6.82 (s, 2H), 2.42 (s, 6H), 2.29 (s, 3H), 1.41 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 142.0, 138.8, 127.4, 83.3, 24.9, 22.1, 21.2 (No C-B Signal). ¹H NMR spectrum included.

(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (Table 1, Entry 13).⁷ Following general procedure A, a mixture of β-bromostyrene (64.1 μL, 91.5 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (2.6 mg, 0.010 mmol) and SPhos (16.4 mg, 0.040 mmol) was heated in 1,4-dioxane for 4 h. Flash column chromatography (2.5% EtOAc/Hexanes) yielded the title compound in 79 mg (69% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.49 (d, J = 8 Hz, 2H), 7.41 (d, J = 18 Hz, 1H), 7.29-7.36 (m, 3H), 6.18 (d, J = 18 Hz, 1H), 1.33 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 149.5, 137.4, 128.9, 128.5, 127.0, 126.5, 83.3, 24.8. ¹H NMR spectrum included.

1-acetyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (Table 1, Entry 14). Following general procedure A, a mixture of *N*-acetyl-5-bromoindole (119 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (2.6 mg, 0.010 mmol) and SPhos (16.4 mg, 0.040 mmol) was heated in 1,4-dioxane for 4 h. Flash column chromatography (15% EtOAc/Hexanes) yielded the title compound in 138 mg (97% yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ: 8.41 (d, J = 7 Hz, 1H), 8.06 (s, 1H), 7.80 (d, J = 7 Hz, 1H), 7.40 (d, J = 2 Hz, 1H), 6.63 (d, J = 2 Hz, 1H), 2.63 (s, 3H), 1.37 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 168.7, 137.4, 131.4, 129.8, 125.2, 115.8, 109.4, 83.7, 24.9, 24.1 (No C-B Signal). IR (neat, cm⁻¹): 3149, 3109, 2978, 1712, 1610, 1539, 1471, 1430, 1352, 1231, 1145. Anal. Calcd. for C₁₆H₂₀BNO₃: C, 67.39; H, 7.07. Found C, 67.15; H, 7.08. ¹H and ¹³C NMR spectrum included.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-1*H*-pyrrole (Table 1, Entry 15).⁸ Following general procedure A, a mixture of 3-bromo-1-(triisopropyl-silanyl)-1*H*-pyrrole⁹ (156 mg, 0.50 mmol), pinacol borane, NEt₃, PdCl₂(CH₃CN)₂ (2.6 mg, 0.010 mmol) and SPhos (16.4 mg, 0.040 mmol) was heated in

⁷ Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 3127.

⁸ Billingsley, K. L.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358-3366.

⁹ Alzare, A.; Guzman, A.; Ruiz, A.; Velards, E.; Muchowski, J. *J. Org. Chem.* **1992**, *57*, 1653-1656.

1,4-dioxane with stirring for 4 h. Flash column chromatography (15% EtOAc/Hexanes) yielded the title compound in 119 mg (74% yield) as a light yellow solid, m.p. 59 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.24 (dd, J = 2,1 Hz, 1H), 6.81 (dd, J = 3,2 Hz, 1H) 6.63 (dd, J = 3,1 Hz, 1H), 7.00 (dd, J = 7,1 Hz, 1H), 1.46 (sept, J = 7 Hz, 3H), 1.33 (s, 12H), 1.09 (d, J = 7 Hz, 18H). ¹³C NMR (75 MHz, CDCl₃) δ: 133.6, 124.9, 115.6, 110.0, 82.6, 24.8, 17.7, 11.6. ¹H NMR spectrum included.

***N,N*-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, Entry 16).**² Following general procedure B, a mixture of 3-chloro-*N,N*-dimethylaniline (77.8 mg, 0.50 mmol), pinacol borane, NEt₃ (0.50 mL), PdCl₂(CH₃CN)₂ (3.9 mg, 0.015 mmol) and SPhos (24.6 mg, 0.060 mmol) was heated with stirring for 24 h. Flash column chromatography (10% EtOAc/Hexanes) yielded the title compound in 99 mg (80% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.27 (t, J = 8 Hz, 1H), 7.19-7.22 (m, 2H), 6.87 (dd, J = 8,3 Hz, 1H), 2.97 (s, 6H), 1.35 (s, 12 H). ¹³C NMR (75 MHz, CDCl₃) δ: 150.1, 128.5, 123.2, 118.6, 115.8, 83.6, 40.8, 24.8 (No C-B Signal). ¹H NMR spectrum included.

2-(2,5-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 17).¹⁰ Following general procedure B, a mixture of 2-chloro-*p*-xylene (67.0 μL, 70.3 mg, 0.50 mmol), pinacol borane, NEt₃ (0.50 mL), PdCl₂(CH₃CN)₂ (3.9 mg, 0.015 mmol) and SPhos (24.6 mg, 0.060 mmol) was heated with stirring for 24 h. Flash column chromatography (2.5% EtOAc/Hexanes) yielded the title compound in 101 mg (87% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.60 (s, 1H), 7.15 (d, J = 8 Hz, 1H), 7.08 (d, J = 8 Hz, 1H), 2.52 (s, 3H), 2.32 (s, 3H), 1.36 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 141.7, 136.3, 133.9, 131.5, 129.8, 83.3, 24.8, 21.7, 20.8 (No C-B Signal). ¹H NMR spectrum included.

4,4,5,5-tetramethyl-2-(thiophen-3-yl)-1,3,2-dioxaborolane (Table 1, Entry 18).¹¹ Following general procedure B, a mixture of 3-chlorothiophene (59.2 mg, 46.4 μL, 0.50 mmol), pinacol borane, NEt₃ (0.50 mL), PdCl₂(CH₃CN)₂ (3.9 mg, 0.015 mmol) and SPhos (24.6 mg, 0.060 mmol) was heated with stirring for 24 h. Flash column

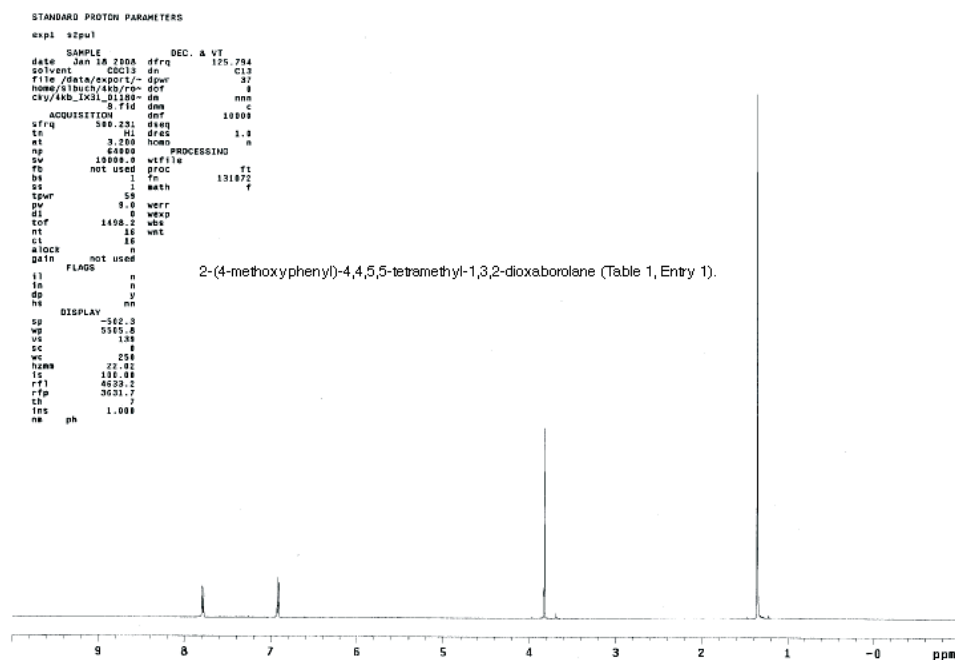
¹⁰ Thompson, A. L. S.; Kabalka, G. W.; Akula, M. R.; Huffman, J. W. *Synthesis* **2005**, 4, 547.

¹¹ Koolmeister, T.; Södergren, M.; Scobie, M. *Tetrahedron Lett.* **2002**, 43, 5965.

chromatography (2.5% EtOAc/Hexanes) yielded the title compound in 62 mg (59% yield) as brown solid, mp 55-56 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.92 (dt, J = 1,3 Hz, 1H), 7.41 (dt, J = 1,5 Hz, 1H), 7.34 (dt, J = 3,5 Hz, 1H), 1.33 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 131.2, 132., 126.1, 103.8, 84.4, 25.6. ¹H NMR spectrum included.

2-cyclopentenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 19).¹²

Following general procedure B, a mixture of 1-chlorocyclopentene (49.6 μL, 51.3 mg, 0.50 mmol), pinacol borane, NEt₃ (0.50 mL), PdCl₂(CH₃CN)₂ (3.9 mg, 0.015 mmol) and SPhos (24.6 mg, 0.060 mmol) was heated with stirring for 24 h. Flash column chromatography (2.5% EtOAc/Hexanes) yielded the title compound in 71 mg (73% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 6.54 (t, J = 2 Hz, 1H), 2.37-2.41 (m, 4H), 1.83 (pent, J = 7 Hz, 2H), 1.28 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ: 147.6, 83.0, 34.7, 34.5, 24.8, 23.9. ¹H NMR spectrum included.



¹² Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001.

STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE DEC. & VT

date Mar 3 2008 dfrq 125.794

solvent CDCl3 dm C13

file /data/export/- spwr 37

home/sibuch/442/rp- dof 0

ckv/4kb_1x57C_8303- dm nnn

ckv/4kb_1x57C_8303- dm c

ACQUISITION dm 10000

sfrq 500.231 dseq

in 41 dres 1.0

at 3.200 homo n

np 64000 PROCESSING

sw 10000.0 vtfile ft

fb not used proc 131872

bs 1 fn f

ss 1 math

tpr 50

pw 9.0 verr

d1 8 vds

tof 1498.2 vbs

nt 16 vnt

ct 14

clock not used

gain not used

ll n

in n

dp v

hs nn

DISPLAY

sp -514.5

wp 5519.8

vc 132

ec 8

wc 258

h2m 72.08

ts 108.08

rfi 4622.3

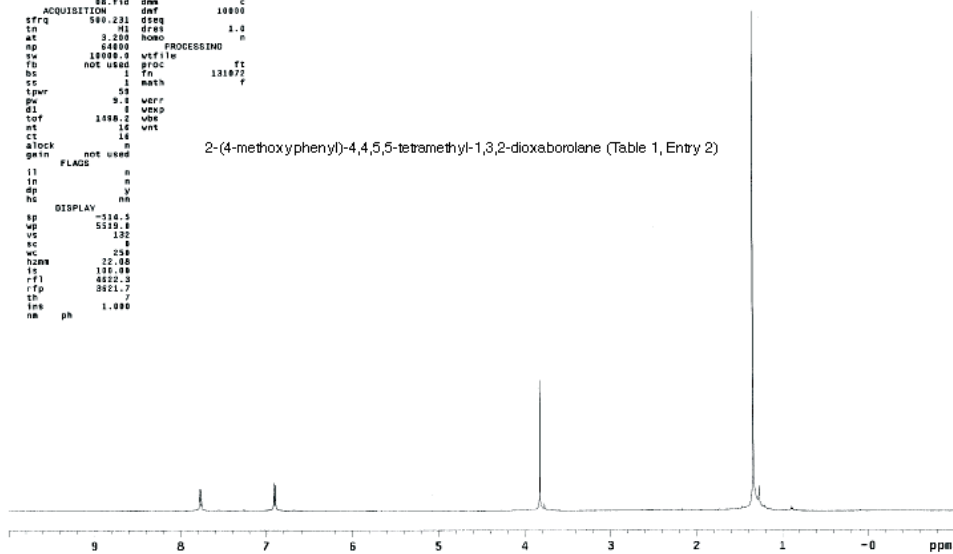
rfp 3621.7

th 7

ims 1.000

nb ph

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 2)



STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE DEC. & VT

date Jan 26 2008 dfrq 125.794

solvent CDCl3 dm C13

file /data/export/- spwr 37

home/sibuch/442/rp- dof 0

ckv/4kb_1x57C_8303- dm nnn

ckv/4kb_1x57C_8303- dm c

ACQUISITION dm 10000

sfrq 500.231 dseq

in 41 dres 1.0

at 3.200 homo n

np 64000 PROCESSING

sw 10000.0 vtfile ft

fb not used proc 131872

bs 1 fn f

ss 1 math

tpr 50

pw 9.0 verr

d1 8 vds

tof 1498.2 vbs

nt 16 vnt

ct 14

clock not used

gain not used

ll n

in n

dp v

hs nn

DISPLAY

sp -514.5

wp 5519.8

vc 132

ec 8

wc 258

h2m 72.08

ts 108.08

rfi 4622.3

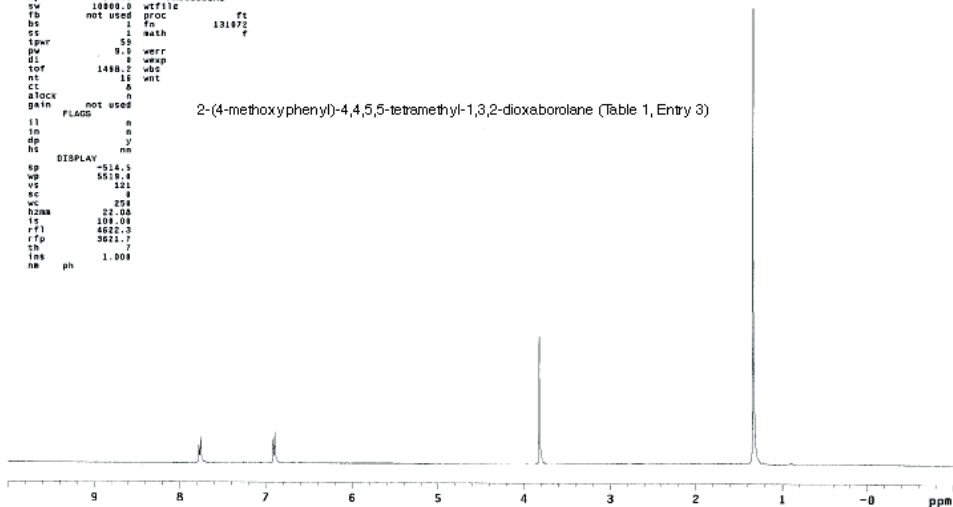
rfp 3621.7

th 7

ims 1.000

nb ph

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 3)

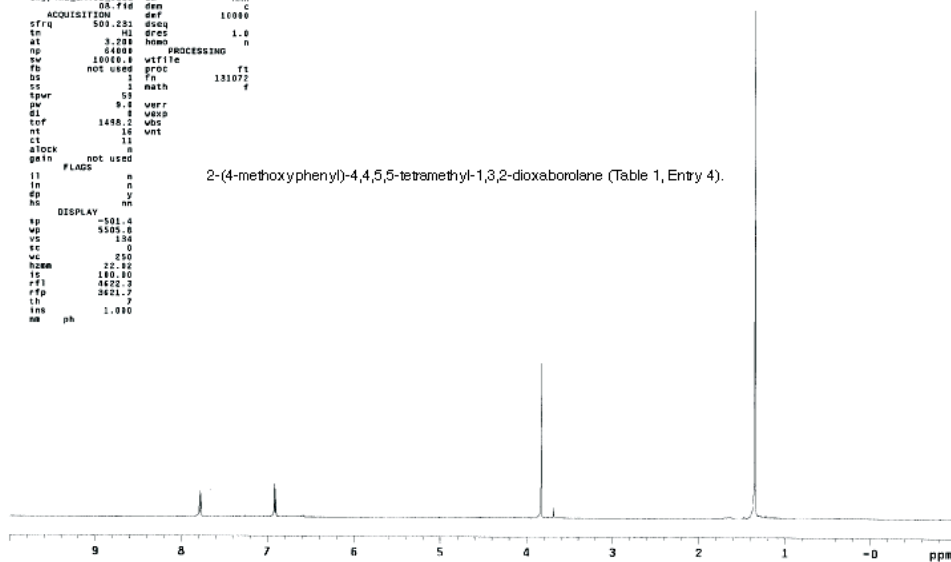


STANDARD PROTON PARAMETERS

exp1 szpul

SAMPLE DEC. & VT
 date Jan 18 2008 dfrq 125.784
 solvent CDCl3 dm C13
 file /data/export/- dpwr S7
 home/sibuch/akb/ro- dof 0
 cxy/4kb_2x48b_1118- dm nnn
 ACQUISITION dm f1d dm c
 cfrq 500.251 dseq 10000
 in H1 drc 1.0
 at 3.288 homo n
 np 64000 PROCESSING
 sv 10000.0 wfile f1
 fb not used proc f1
 bs 1 fn 131072
 ss 1 math f
 tpmr 50
 pw 9.8 verr
 el 8 versa
 totf 1498.2 vbs
 nt 16 vnt
 ct 11
 alock n
 gain not used
 FLAGS
 l1 n
 in n
 ep y
 hs nn
 DISPLAY
 sp -501.4
 wp 5585.8
 vs 138
 vc 0
 uc 250
 hzmm 22.02
 te 189.80
 rff 4672.3
 rfp 3631.7
 th
 tns ph 1.000
 na

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 4).

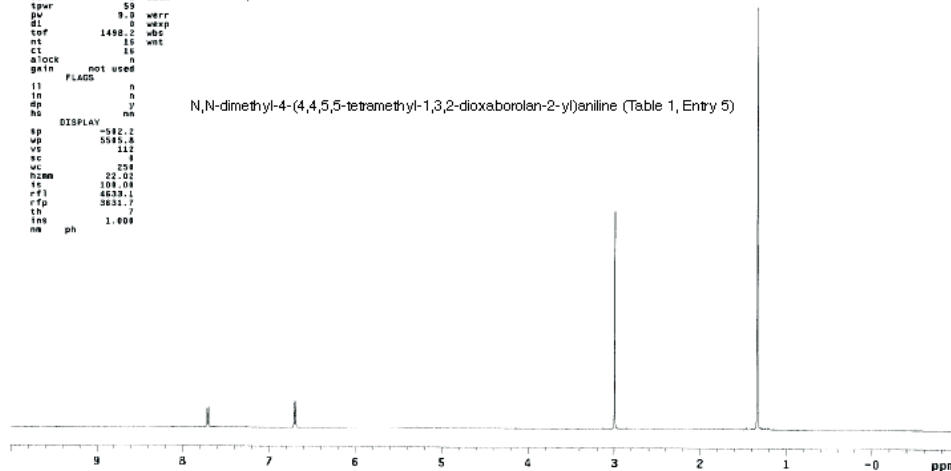


STANDARD PROTON PARAMETERS

exp1 szpul

SAMPLE DEC. & VT
 date Jan 22 2008 dfrq 125.784
 solvent CDCl3 dm C13
 file /data/export/- dpwr S7
 home/sibuch/akb/ro- dof 0
 cxy/4kb_2x48b_1118- dm nnn
 ACQUISITION dm f1d dm c
 cfrq 500.251 dseq 10000
 in H1 drc 1.0
 at 3.200 homo n
 np 64000 PROCESSING
 sv 10000.0 wfile f1
 fb not used proc f1
 bs 1 fn 131072
 ss 1 math f
 tpmr 50
 pw 9.8 verr
 el 8 versa
 totf 1498.2 vbs
 nt 16 vnt
 ct 11
 alock n
 gain not used
 FLAGS
 l1 n
 in n
 ep y
 hs nn
 DISPLAY
 sp -502.2
 wp 5585.8
 vs 112
 vc 0
 uc 250
 hzmm 22.02
 te 189.80
 rff 4672.3
 rfp 3631.7
 th
 tns ph 1.000
 na

N,N-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, Entry 5)

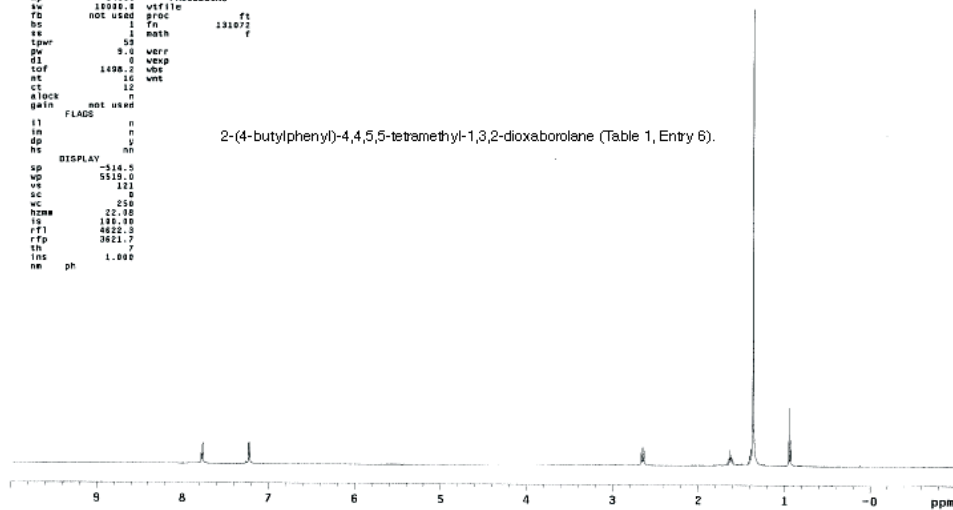


STANDARD PROTON PARAMETERS

exp1 s2pu1

SAMPLE DEC. & VT
 date Jan 22 2008 dfrq 125.794
 solvent CDCl3 dn C13
 file /data/export/- dpwr 37
 home/s1buck/4kb/r0- dof 0
 cky/4kb_2X56_01228- dm nnn
 c dm c
 ACQUISITION dm 18000
 sfrq 500.231 dseq
 tn H1 drcs 1.0
 at 3.200 homo n
 np 64000 PROCESSING
 sw 18000.0 vtf10
 tn not used proc f1
 ds 1 f1 131072
 ss 1 math f
 tpr 50
 pw 9.0 verr
 d1 0 wds
 tof 1408.2 wds
 nt 16 wnt
 ct 12
 a lock n
 gain not used
 FLAGS
 f1 n
 tn n
 dp y
 ds nn
 DISPLAY
 sp -514.5
 wp 5519.0
 vs 121
 sc 0
 wc 258
 hzmm 22.02
 ts 130.08
 rfi 4622.3
 rfp 3621.7
 th
 rms ph 1.000

2-(4-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 6).

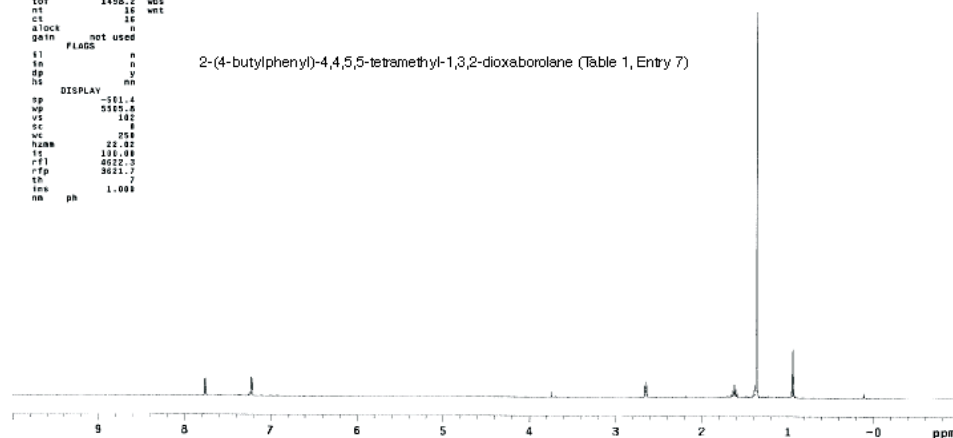


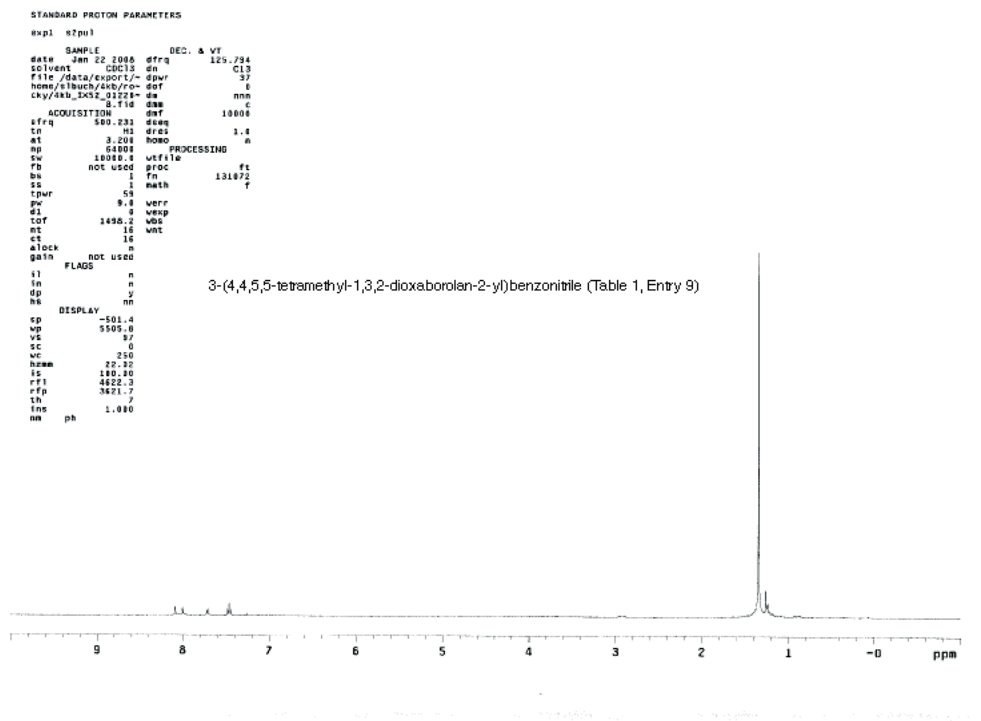
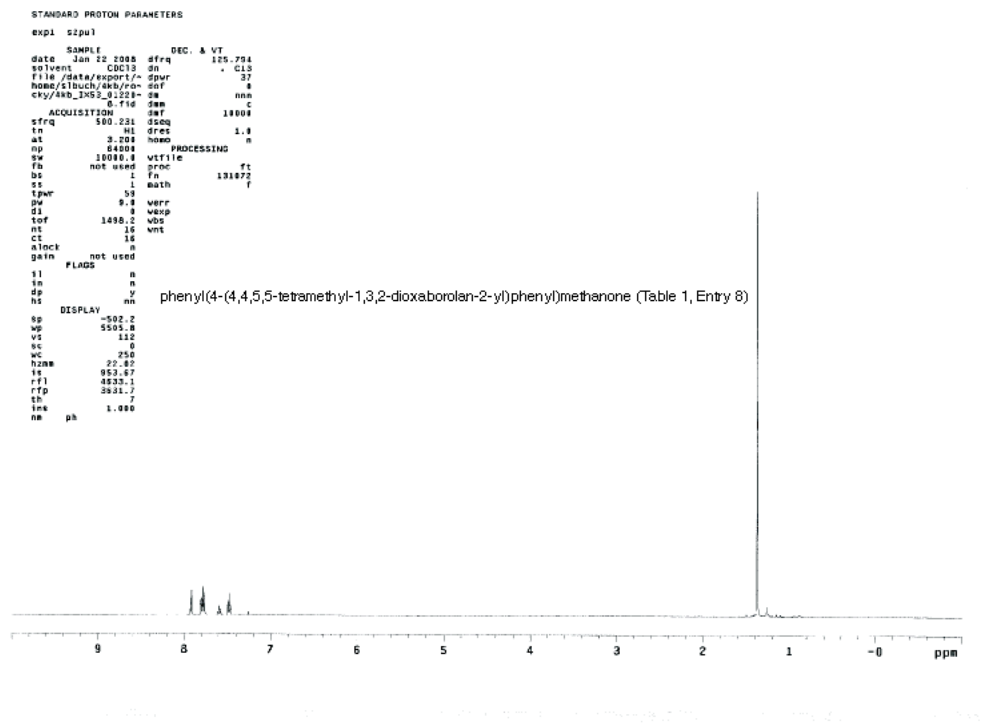
STANDARD PROTON PARAMETERS

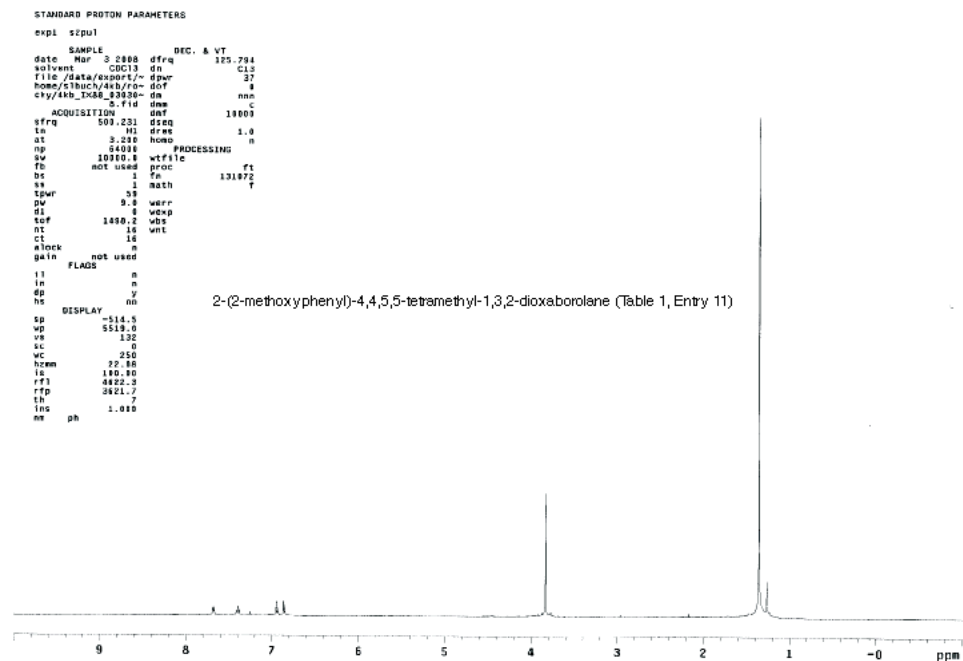
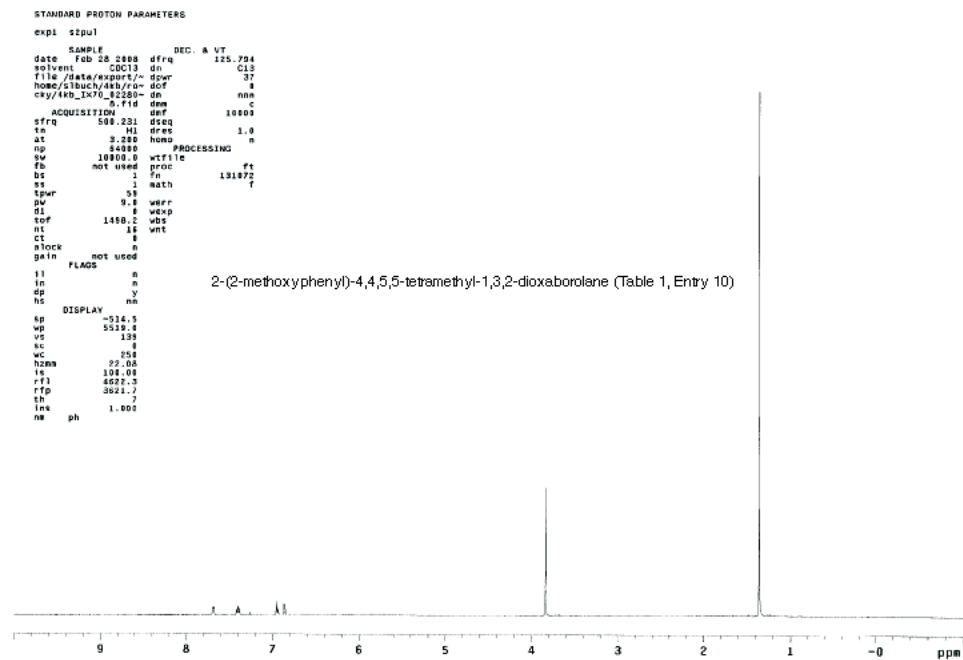
exp1 s2pu1

SAMPLE DEC. & VT
 date Jan 18 2008 dfrq 125.794
 solvent CDCl3 dn C13
 file /data/export/- dpwr 37
 home/s1buck/4kb/r0- dof 0
 cky/4kb_2X45_01189- dm nnn
 c dm c
 ACQUISITION dm 18000
 sfrq 500.231 dseq
 tn H1 drcs 1.0
 at 3.200 homo n
 np 64000 PROCESSING
 sw 18000.0 vtf10
 tn not used proc f1
 ds 1 f1 131072
 ss 1 math f
 tpr 50
 pw 9.0 verr
 d1 0 wds
 tof 1408.2 wds
 nt 16 wnt
 ct 16
 a lock n
 gain not used
 FLAGS
 f1 n
 tn n
 dp y
 ds nn
 DISPLAY
 sp -501.4
 wp 5505.8
 vs 182
 sc 0
 wc 258
 hzmm 22.02
 ts 130.08
 rfi 4622.3
 rfp 3621.7
 th
 rms ph 1.000

2-(4-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 7)







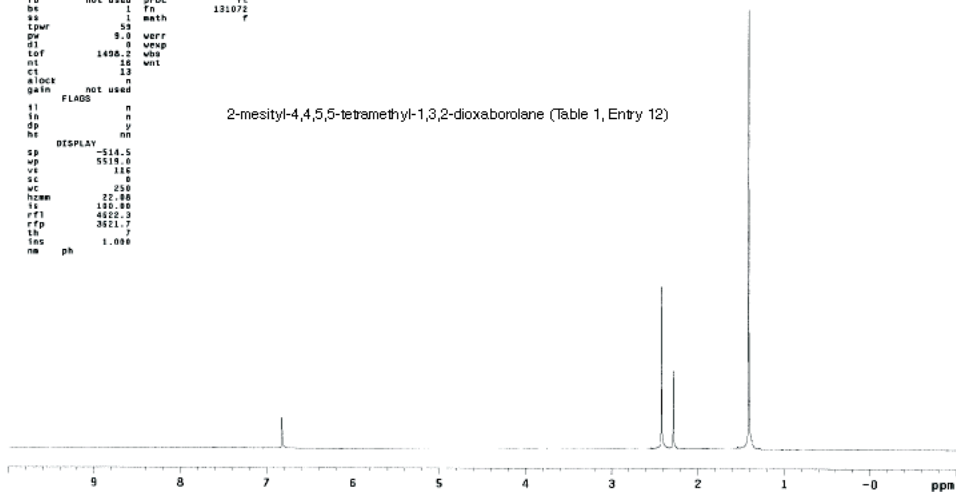
STANDARD PROTON PARAMETERS

```

exp1 62pu1
SAMPLE DEC. & VT
date Jan 12 2008 dfrq 125.794
solvent CDCl3 dm C13
file /data/export/- dpwr 37
home/sibuch/465/ro- dof 0
ckv/4kb_1x05_01051- dm nnn
0. f10 dm 18000
ACQUISITION dof
sfreq 500.231 dseq 1.8
in H1 drcd
at 3.208 homo n
np 64000 PROCESSING
sw 10000.8 vtf1le
fn not used proc fc
bs 1 fn 131072
ss 1 math f
tpr 50
pw 9.0 verr
el 8 verrp
tof 1498.2 vbs
nt 16 vnt
ct 16
clock n
gain not used
FLAGS
il n
in n
sp y
hs nn
DISPLAY
sp -518.5
up 5519.6
vs 116
sc 0
uc 250
hzmw 22.80
ts 180.00
rfl 4622.3
rfp 3821.7
th 1.000
ns
nm ph

```

2-mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 12)



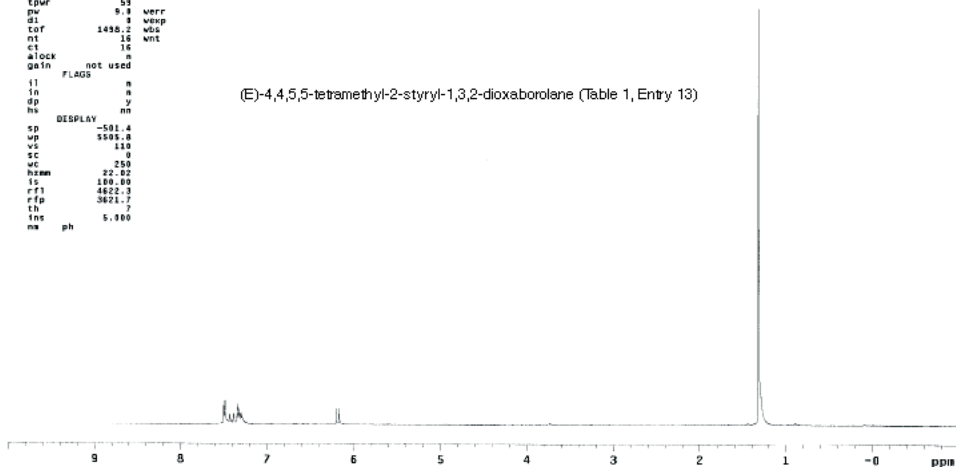
STANDARD PROTON PARAMETERS

```

exp1 62pu1
SAMPLE DEC. & VT
date Jan 26 2008 dfrq 125.794
solvent CDCl3 dm C13
file /data/export/- dpwr 37
home/sibuch/465/ro- dof 0
ckv/4kb_1x05_01051- dm nnn
0. f10 dm 18000
ACQUISITION dof
sfreq 500.231 dseq 1.8
in H1 drcd
at 3.208 homo n
np 64000 PROCESSING
sw 10000.8 vtf1le
fn not used proc fc
bs 1 fn 131072
ss 1 math f
tpr 50
pw 9.0 verr
el 8 verrp
tof 1498.2 vbs
nt 16 vnt
ct 16
clock n
gain not used
FLAGS
il n
in n
sp y
hs nn
DISPLAY
sp -501.4
up 5505.8
vs 110
sc 0
uc 250
hzmw 22.82
ts 180.00
rfl 4622.3
rfp 3821.7
th 5.900
ns
nm ph

```

(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (Table 1, Entry 13)



STANDARD PROTON PARAMETERS

exp1 s2pul

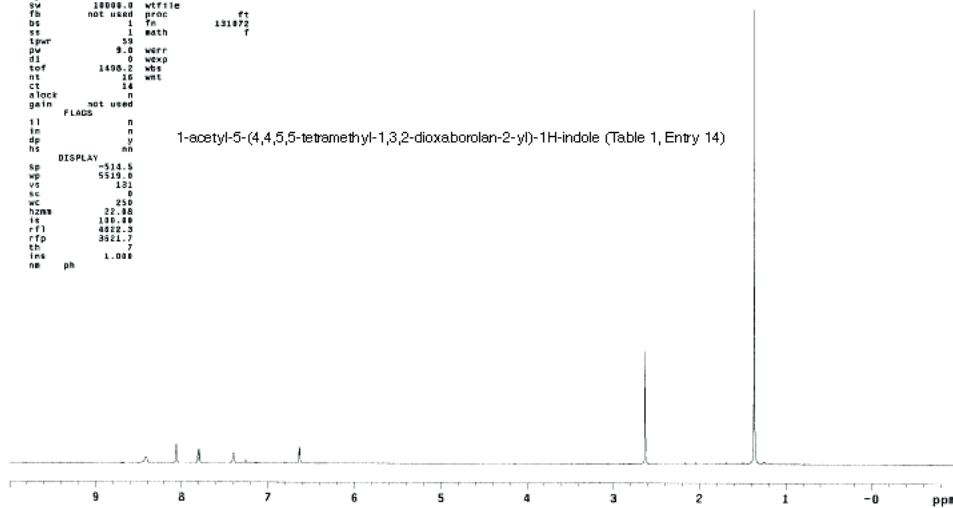
SAMPLE DEC. & VT
 date Jan 19 2008 dfrq 125.794
 solvent CDCl3 dn C13
 file /data/export/~ gpar 37
 home/sibuch/4ks/ro- got 8
 cpy/4ks_incl_0128- de non
 0. fid dm 1000
 C

ACQUISITION
 sfrq 500.231 dseq 1.0
 tn 81 dres
 at 3.200 homo n
 np 64000 PROCESSING
 pw 10000.0 wtfle
 fb not used proc ft
 bs 1 tn 131872
 ss 1 math f
 tpuw 50
 pw 9.0 wvrr
 di 0 wexp
 tof 1406.2 wbs
 nt 16 wnt
 ct 16
 alock n
 gain not used

FLAGS
 ti n
 in n
 dp y
 hs nn

DISPLAY
 sp -518.5
 wp 5519.0
 vs 101
 sc 0
 wc 250
 hzmm 22.88
 is 131.88
 rfi 4512.3
 rfp 3521.7
 th 13
 ins 1.000
 ne ph

1-acetyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (Table 1, Entry 14)



STANDARD CARBON PARAMETERS

exp2 s2pul

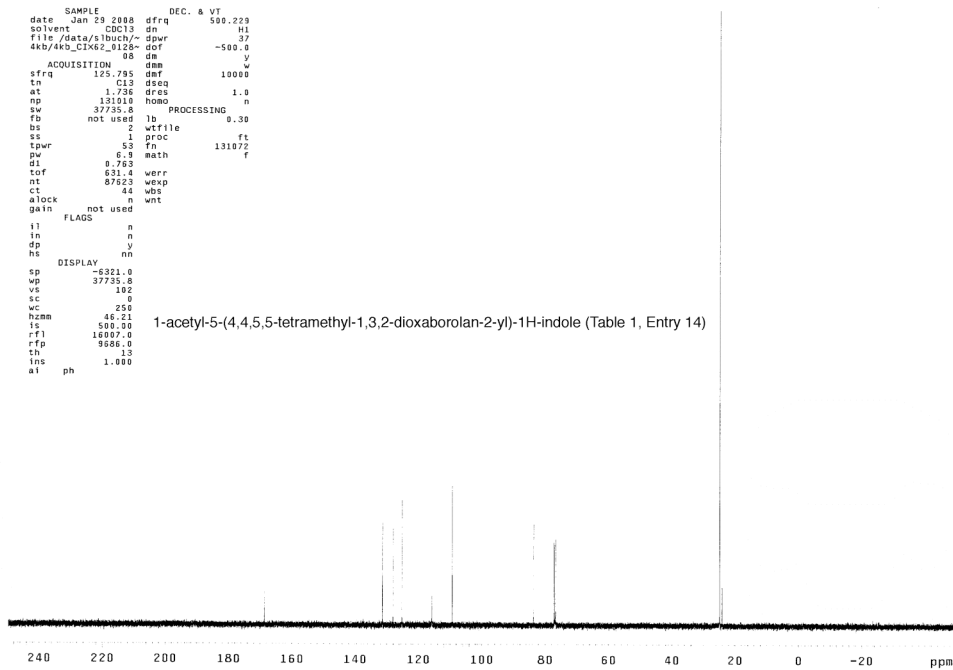
SAMPLE DEC. & VT
 date Jan 29 2008 dfrq 500.229
 solvent CDCl3 dn H1
 file /data/sibuch/~ gpar 37
 4ks/4ks_incl_0128- got -500.0
 08 dm y
 w

ACQUISITION
 sfrq 125.795 dmf 10000
 tn 013 dseq
 at 1.738 dres 1.0
 np 131010 homo n
 pw 37735.5 PROCESSING
 fb not used lb 0.30
 bs 1 proc ft
 tpuw 50 fn 131072
 pw 6.5 math f
 di 0.763
 tof 631.4 wvrr
 nt 87623 wexp
 ct 64 wbs
 alock n wnt
 gain not used

FLAGS
 ti n
 in n
 dp y
 hs nn

DISPLAY
 sp -5321.0
 wp 37735.0
 vs 102
 sc 0
 wc 250
 hzmm 46.21
 is 500.00
 rfi 16007.0
 rfp 9886.0
 th 13
 ins 1.000
 al ph

1-acetyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (Table 1, Entry 14)



STANDARD PROTON PARAMETERS

```

expt 12pul

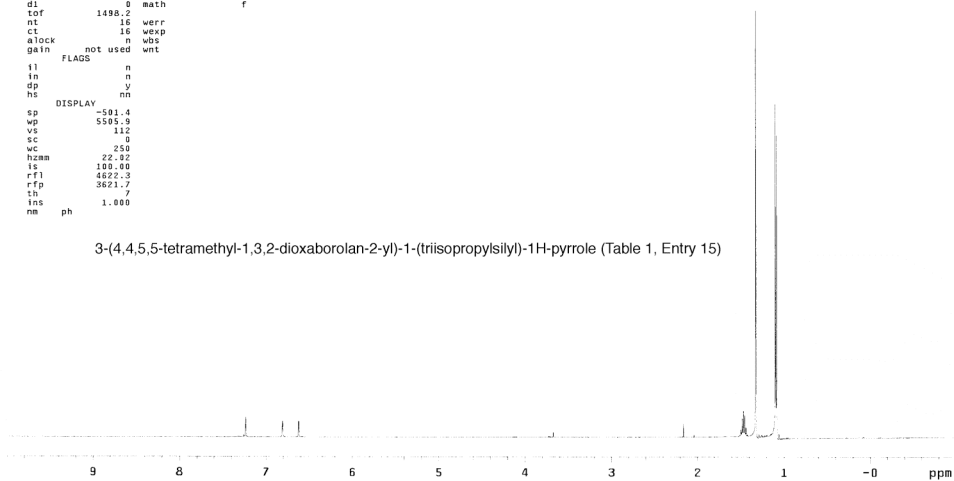
SAMPLE
date Mar 5 2008 dfrq 125.794
solvent CDCl3 dm C13
file /data/export/- dpar 37
ACQUISITION exp ddf 0
sfreq 500.231 dm nnn
tn 101 dmf 10000
at 3.200 dmf 10000
np 64000 dseq 1.0
sw 10000.0 dres 1.0
fb not used homo n
bs 1 PROCESSING
ss 1 wfile ft
tpr 50 proc f
pw 9.0 fn 131072
dl 0 math f
tof 1498.2
nt 16 verr
ct 16 vexp
alock n vbs
gain not used vnt

FLAGS
il n
in n
dp y
hs nn

DISPLAY
sp -591.4
wp 5595.9
vs 112
sc 0
wc 250
hzmm 22.02
ls 100.00
rf1 4622.3
rfp 3621.7
tn 7
ins ph 1.000
nm

```

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-1H-pyrrole (Table 1, Entry 15)



STANDARD PROTON PARAMETERS

```

expt 12pul

SAMPLE
date Mar 3 2008 dfrq 125.794
solvent CDCl3 dm C13
file /data/export/- dpar 37
homer/touch/46b/10- ddf 3
cty/14h_1505_51810- dm nnn
ACQUISITION 5.fid dmf 10000
sfreq 500.231 dseq 1.0
tn 101 dres 1.0
at 3.200 homo n
np 64000 PROCESSING
sw 10000.0 wfile ft
fb not used proc f
bs 1 fn 131072
ss 1 math f
tpr 50
pw 9.0 verr
dl 0 vexp
tof 1498.2 vbs
nt 16 vnt
ct 16
alock n
gain not used

FLAGS
il 0
in n
dp y
hs nn

DISPLAY
sp -591.2
wp 5595.8
vs 104
sc 0
wc 250
hzmm 22.02
ls 100.00
rf1 4622.3
rfp 3621.7
tn 7
ins ph 1.000
nm

```

N,N-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, Entry 16)

